DDT, chlordane and hexachlorobenzene in the air of the Pearl River Delta revisited: a tale of source, history and monsoon

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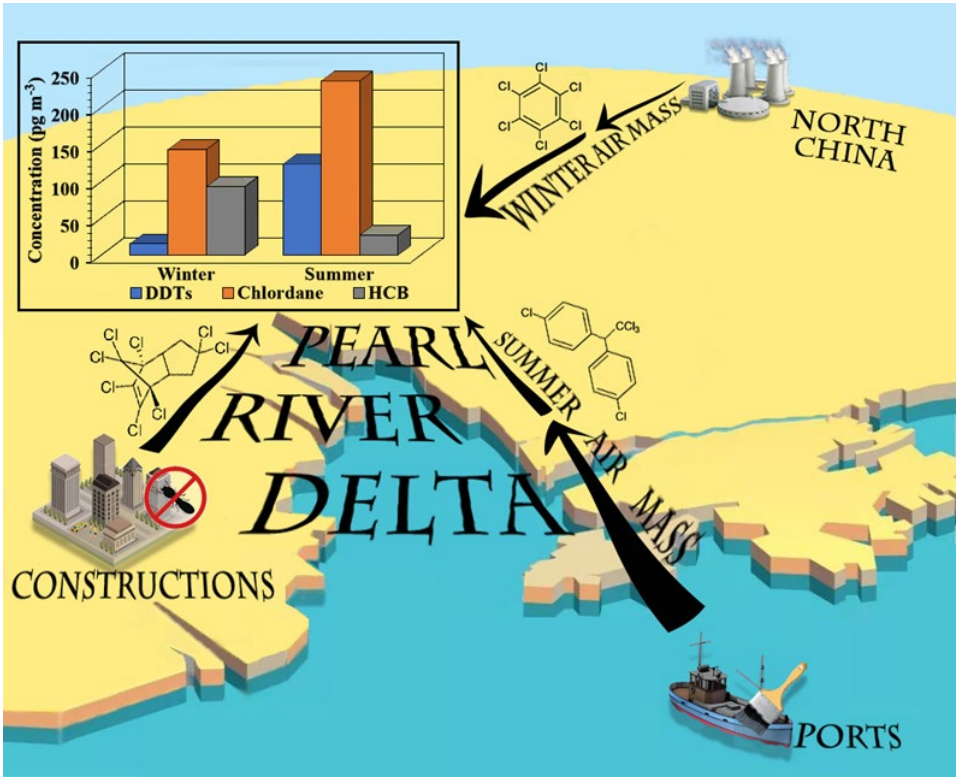

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Abstract

Although organochlorine pesticides (OCPs) have been banned for more than three decades, their concentrations decreased slowly largely owing to their environmental persistency, illegal application and exemption usage. A revisit would be of great interest in assessing the current regional situation of DDT, chlordane and hexachlorobenzene (HCB), which were first enlisted by Stockholm Convention tracked back to the year of 2001. An air sampling campaign was carried out during 2017-2018 in nine cities of the Pearl River Delta (PRD), where the historical application of DDT and chlordane was most intensive in China. Different seasonality was observed with the three types of OCP compounds. DDT displayed higher concentrations in summer than that in winter. Chlordane showed minor seasonal variation, while HCB prevailed in winter. Technical DDT compositions still dominated, signaling a still-existing illegal usage of DDT in antifouling paint for fishing ships during the fish suspension period in summer, while excluding almost the dicofol-type DDT. Chlordane may emit into the air by kinetically-limited release from historic building foundations and dams, rather than by temperature-controlled evaporation from surface soil. HCB was unintentionally-produced by combustion transported from the north in winter. The unique coupling of summer monsoon with paint DDT usage, winter monsoon with combustion HCB emission, as well as the historical 'sealed' chlordane jointly presented the dynamic picture of these OCP compounds in the air of the PRD. Their back-calculated annual emission rates accounted for insignificant contribution to the nationally documented production (<1‰). Our study showcased that a geographic-anthropogenic scene, including source, history and air circulation patterns, would be specifically set for a comprehensive understanding of the fate of OCP compounds in a region.

Keywords: ??

Introduction

Organochlorine Pesticides (OCPs) are firstly regulated as the "Dirty Dozen" of persistent organic pollutants (POPs) by the Stockholm Convention,[1] because they are environmentally persistent, will undergo long-range atmospheric transport (LRAT), and bioaccumulate in the food chain, indicating threat to ambient environment and human health.[2] Though more than three decades passed, they are not declining rapidly as expected[3] and still widely detected around the world,[4-8] even in remote regions, such as in the air and soil of Tibet Plateau,[9, 10] and deep sea[11] and local population[12] of the Arctic. The slowly decreasing and relatively stable trend of OCPs is caused by their inherent persistency, illegal application,[13] and exemption usage on public health.[14] In Africa, DDT was reintroduced to control malaria by indoor residual spraying (IRS) and has caused increased exposure to local population.[15, 16]

China is the world's second largest pesticides producer[3] and OCPs accounted for about 80% of national pesticides production during 1950s-1970s.[2] DDT, chlordane and HCB were selected as model compounds here, due to their historical extensive application in China. DDT was widely used on cotton fields in China from 1950s and banned in 1983, with historical production of 0.4 million tonnes, accounting for 20% of the global production.[3] After its ban, it's still used in antifouling paint for fishing ships until 2009[13] and dicofol production until 2019.[17] As a country with the most server termite damage, chlordane was produced in high volume in China for termite prevention and control.[2, 18] Small amount of chlordane was used in agricultural in China until its ban on all crops in 1996.[19] But most chlordane was used to protect new construction from termite damage since 1978 and banned for all purposes in 2009, accounting for up to 95% of China's total chlordane production.[19] HCB is not only from its industrial and agricultural application, but also produced as an unintentionally byproduct during the industrial manufacture and combustion processes.[20] In China, it was never directly used as a pesticide, but as an intermediate to produce chlorothalonil,[21] pentachlorophenol (PCP) and pentachlorophenol-Na (PCP-Na).[2] Recent study indicated that it's almost entirely originated from combustion, such as metallurgical thermal process and biomass burning.[22]

Located in the subtropical region of southern China, the Pearl River Delta (PRD) is one of the most developed regions in China and has the most extensive pesticides application history of

this country.[3] Therefore, the PRD is often regarded as a significant source of OCPs under the global context.[23] During 2000s, we have conducted several OCPs monitoring and surveillance projects in the air of PRD region using both active [23] and passive [24] air samplers. A revisit would be of great interest in assessing the current regional situation of DDT, chlordane and hexachlorobenzene (HCB), which were first enlisted by Stockholm Convention tracked back to the year of 2001. Meanwhile, this study is under the framework of the National Key R&D Program of China Towards an Air Toxic Management SYstem (ATMSYC) in China.

In this study, the ambient air was selected as the sampling medium, since it is easy to practice in field, well-mixed to present regional pollution with high temporal and spatial resolution. Therefore, we aimed to: 1) determine the occurrence, spatial distribution, seasonal variation of selected OCPs (HCB, DDTs and chlordane) in PRD, representing a typical rapidly developed region of China ; 2) gain new insights on their current status of regional sources and input pathway under a geographic-anthropogenic scene; 3) evaluate the effectiveness of Stockholm Convection and shed lights on the sound management of banned OCPs.

Materials and Methods

PRD region

The PRD is one of the most developed Chinese city clusters, located in south coast of China. It covers 0.4% of national land area, but contains 8% of the country's population.[25, 26] The PRD is a representative geographic locus of China's rapid urbanization since the implementation of the "Reform and Opening Up" policy in 1978.[25] In 2019, Chinese policymakers released the blueprint for the development of Greater Bay Area (GBA), to build a world-class city cluster across Guangdong-Hong Kong- Macau region and transform it into a new technology and innovation hub. Thus, the PRD has witnessed the most rapid urban expansion in human history – a predominantly agricultural region transforming into the world's largest city cluster.

However, it is of great concern in terms of air quality in PRD region over the past decades because of rapidly increased fossil fuel consumption associated with industrialization and urbanization. The PRD is in the subtropical zone under strong influence of Asian monsoon.[23] Due to its unique climate and weather, this region has complex atmospheric circulation, which

plays important roles in transport and redistribution of air pollutants. The convergence of cold air from the north and warm air from the south would cause the accumulation of air pollutants in PRD.[27]

Sampling campaign

In total, we selected nine prefecture-level cities of PRD, which are Shenzhen, Foshan, Dongguan, Zhongshan, Jiangmen, Zhuhai, Zhaoqing, Huizhou and Guangzhou, as detailed in Table S1 and Fig. S1. All utilized sampling sites are official monitoring stations, which were carefully selected to represent the city-level air pollution characteristics. At each site, a high-volume active air sampler (Mingye Instruments Co., Guangzhou, China) was fitted with polyurethane foam plugs (PUF, 14 cm in diameter×7.5 cm in thickness, 0.030 g/cm^3 in density) and quartz fiber filter (QFF, Whatman, 203 mm×254 mm), to capture both gas phase pollutants and $PM_{2.5}$ samples. 24h air samples were collected for one week in winter (January to February 2018) and in summer (July to August 2018), respectively. Therefore, each city obtained seven paired air samples. Overall, a total of 126 paired samples were collected in the nine cities during the sampling periods. Prior to sampling, QFFs were baked at 450℃ overnight and PUFs were pre-cleaned separately with acetone and dichloromethane (DCM). All the samples were delivered to the lab and stored at -20℃ before analysis.

Sample pretreatment and analysis

The detailed methods for sample treatment and instrumental analysis are given in previous studies.[6, 22] In short, QFFs and PUFs were spiked with ^{13}C labeled *trans*-chlordane as the recovery surrogate and extracted in a Soxhlet apparatus for 24h with DCM. The extracts were concentrated via rotary evaporation and solvent-exchanged into hexane with reduced volume of 0.5-1 mL. They were then purified by a multilayer acidified silica gel column and concentrated into a vial under gentle nitrogen. $^{13}C_{12}$-labelled PCB 141 was added as internal standards before instrumental analysis. Samples were analyzed on an Agilent 7890A/7000A GC-MS/MS with a CP-Sil 8 CB column (50 m × 0.25 mm × 0.12 μm) in a multiple reaction monitoring (MRM) mode. The precursor/product ions and retention time are listed in Table S2.

Quality assurance and quality control (QA/QC)

QA/QC was conducted using field blanks, procedural blanks and surrogates spiked recoveries. Most congeners were not detected in the field blanks and procedural blanks. The average recovery rate of $^{13}C_{12}$ labelled trans-chlordane was 108% ± 22%. The inlet degradation of DDT was checked by injecting p,p'-DDT standard every 10 samples and controlled within 15%. The reported concentration was corrected for blanks and surrogate recovery. The method detection limits (MDLs) were calculated as the average of field blanks plus 3 times their standard deviations. MDLs were assigned as 3 times of instrumental detection limits (IDLs) if a congener was not detected in field and procedural blanks. IDLs were defined as the amounts of analytes generating a signal-to-noise of 3:1 using the lowest standard level, assuming a linear response increase. The IDLs and MDLs for DDTs congeners ranged from 11~71 pg and 0.005-1.11 pg/m^3 as detailed in Table S3.

Backward trajectories simulation and Potential source contribution function (PSCF) model

The backward particle release simulation, considering the dispersion processes in the atmosphere, is widely used to identify the history of air masses.[28] We performed this simulation following previous studies.[28, 29] The backward particle release simulation was carried out using Hybrid Single-particle Lagrangian Integrated Trajectory model (HYSPLIT 4.0) developed by the National Oceanic and Atmospheric Administration (NOAA) (https://ready.arl.noaa.gov/HYSPLIT.php). The input mereological data were obtained from Gridded Meteorological Data Archives of Air Resources Laboratory (ARL) (https://ready.arl.noaa.gov/archives.php). All trajectories were calculated at the interval of 1h and the cluster analysis is presented in Fig S2.

The PSCF model was applied to assess potential source areas with high levels of DDTs, HCB and chlordane. This can be described as a conditional possibility, characterized by the use of trajectories to the sampling sites to determine the spatial distribution of possible geophysical source locations.[30, 31] The ij_{th} component of a PSCF field ($PSCF_{ij}$) is defined as:

$$\mathrm{PSCF}_{ij} = \frac{m_{ij}}{n_{ij}}$$

166 Where n_{ij} represents the number of trajectory endpoints falling in the ij^{th} cell and m_{ij} is the
167 number of air masses, from the same cell, loaded with species whose concentrations are
168 greater than the set criterion values. In this study, the threshold values were set as the 75^{th}
169 percentile of OCPs concentration to identify the potential source areas.

170 **Observation-based back-calculation of emission**

171 We employed a "top-down" approach to retrospectively quantify emissions of target OCP
172 compounds based on a combination of field measurements and modeling, which has been
173 widely applied for industrial chemicals in urban areas worldwide.[32, 33] It overcomes the
174 disadvantage of poor or incomplete emission data required by "bottom-up" approach, based
175 on chemical production, use and disposal data combined with emission factors.[32] A Level IV
176 global-scale multimedia contaminant fate model, the BETR-Global model, was selected to
177 back-calculate the inventory, which has been fully evaluated and extensively used to
178 understand global dynamics of persistent semivolatile pollutants.[34-36] The simulation was
179 performed in Python programming language (http://betrs.sourceforge.net), with a spatial
180 resolution of 3.75° × 3.75° grid cells. Each grid cell contains seven compartments: upper
181 atmosphere, lower atmosphere, vegetation, freshwater, ocean, soil and freshwater
182 sediment.[35]

183 The main input parameters, including physical-chemical properties and environmental half-
184 lives were predefined in the BETR-Global as shown in Table S4. Emission rate into the lower air
185 compartment is the only adjustable parameter, which was adjusted in such a way that the
186 median of the modeled concentrations in lower air of target grid is equal to the median of the
187 measurements as suggested elsewhere.[32] Influenced by Asia monsoon, the PRD mainly
188 receives the upwind from north in winter and from south in summer (Fig S2).The atmospheric
189 monitoring site in Huizhou (the northmost site) and in Shenzhen (the southmost site) was
190 chosen as background stations in winter and in summer, respectively.

Results and discussion

OCPs profile in PRD region

In this study, nine target compounds were determined, including DDTs (sum of o,p-DDT, p,p'-DDT, o,p-DDD, p,p'-DDD, o,p-DDE and p,p-DDE), chlordane (trans-chlordane (TC) and cis-chlordane(CC)) and HCB. The average concentration, detection frequency (DF) of sum level in gas phase and particle phase are summarized in the Table 1 and detailed in Table S5-S6. All measured compounds were predominant in gas phase, accounting for up to 95% of the total concentration in gas and particle phases. Detection rates were low ranging from 5% to 75% in particle samples, while they reached 69-100% in gaseous samples. HCB and chlordane were detected in all gaseous samples. Therefore, only the summed concentrations in gas phase and particle phase were further discussed. In addition, the atmospheric levels of various OCPs ranked as: chlordane>HCB>DDTs in winter and chlordane> DDTs> HCB in summer.

Table 1. Summary of DDTs, chlordane and HCB in the air of nine cities in the PRD region (n=126).

Season	Winter			Summer		
pg/m^3	min	max	Mean±Std	min	max	Mean±Std
HCB	<MDL*	163	92±27	1	63	27±11
cis-Chlordane	1	267	44±65	1	361	71±66
trans-Chlordane	5	641	92±136	5	1070	167±174
CHLs	7	893	144±208	6	1431	236±233
TC/CC	1.7	6.4	2.4±0.6	1.6	4.5	2.3±0.4
o,p'-DDT	<MDL	29	3±7	<MDL	89	30±21
P,P`-DDT	1	87	10±18	9	389	80±74
o,p'-DDD	<MDL	1	0.2±0.2	<MDL	6	2±1
p,p'-DDD	<MDL	2	0.3±0.2	<MDL	10	3±2
o,p'-DDE	<MDL	5	0.2±03	<MDL	5	1±2
p,p'-DDE	<MDL	7	1±2	<MDL	29	7±6
DDTs	2	123	15±27	11	516	124±104
p,p'-DDT/DDTs	0.26	0.87	0.60±0.14	0.33	0.92	0.63±0.09
DDT/DDTs	0.50	0.95	0.80±0.10	0.72	0.97	0.89±0.04
p,p'/o,p-DDT	0.9	38.7	5.1±5.7	0.8	19.7	3.0±2.5
p,p'-DDT/p,p'-DDE	1.0	43.4	9.5±8.1	2.5	94.9	14.1±16.3
HCB/DDTs	0.9	55.4	17.2±11.6	0.03	1.5	0.4±0.3

* MDL is the method detection limit and its specific value is listed in Table S3.

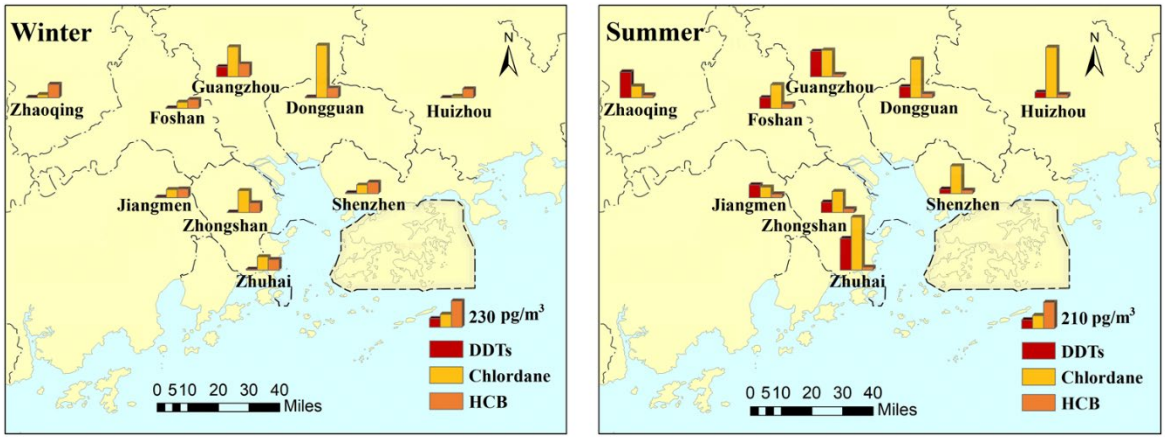


Figure 1. The spatial distributions of DDTs, chlordane and HCB during winter and summer in 9 cities of the PRD, presented as summed concentration in both gas phase and particle phase (pg/m^3). This figure was modified from outputs of ArcGIS 10.3 software, and the base map of China was from http://www.arcgisonline.cn.

DDT

Fig. 1 presents the DDTs distribution of two sampling seasons in PRD region. Relatively high levels of DDTs were observed at most sites in wide range of 2-156 (mean±std: 69±93 pg/m^3) with significant seasonality (Kruskal-Wallis H Test, $p<0.001$). Its concentration in winter was 15±27 pg/m^3, which is one order of magnitude lower than that in summer (124±104 pg/m^3). p,p'-DDT was dominant (>50%) in 87% of samples, contributing averagely 62±12% to ∑DDTs and at the level of 44±64 pg/m^3. High correlation was found among DDT and its metabolites (all $R^2>0.90$, $p<0.001$), particularly for p,p'-DDT and summed DDTs with $R^2=0.99$ ($p<0.001$). In winter of 2017, Guangzhou had the highest DDTs level of 88 ± 30 pg/m^3, which is an order of magnitude higher than that at other sites. This is owing to varied sampling period in Guangzhou, receiving greater portion of air masses from the sea, as shown in Fig. 2c. In summer of 2018, Zhuhai, a southern coastal city, had the highest DDTs with an average of 254±86 pg/m^3.

Chlordane

Chlordane has been widely used for termite control in building foundations, dams, grasslands and forests in China.[23] High chlordane level was observed in both winter and summer in the PRD region, with significant but relatively minor seasonality (Kruskal-Wallis H Test, $p<0.001$).

Chlordane (TC+CC) concentration in summer was 165±169 pg/m^3, which was twice higher than that in winter (99±143 pg/m^3). The annual chlordane levels ranged between 6-1431 (190 ±226) pg/m^3. Its level was drastically fluctuated at the same site with a factor of ten. TC dominated the chlordane family accounting for 61-86%, whilst previously observed CC dominated.[37] Good correlation between TC and CC was observed with R^2=0.95 ($p<0.001$). In winter, the highest and lowest concentrations of chlordane were found in Dongguan (468±339 pg/m^3) and Huizhou (14±12 pg/m^3), respectively. In summer, the highest concentration of chlordane was 426±125 pg/m^3 (Zhuhai), and the lowest concentration was 85±25 pg/m^3 (Jiangmen).

HCB

The annual HCB concentration in PRD region was in a wide variation of 1-163 (60±39) pg/m^3. Contradictory to the seasonality of DDTs, HCB concentration in winter (93±27 pg/m^3) was triple times that in summer (27±12 pg/m^3), with a significant seasonal difference (Kruskal-Wallis H Test, $p<0.001$). The HCB level was more stable in the same season than DDT and chlordane, indicating well-mixed air masses. In winter, the highest concentration of HCB was 120±34 pg/m^3 in Zhaoqing, and the lowest concentration was 78±24 pg/m^3 in Jiangmen.

Comparison with other studies

The comparison of DDTs, chlordane and HCB with the literature is summarized in Table S7. In the PRD region, DDTs, chlordane and HCB rapidly decreased to different extents since previous surveys in 2000s.[23, 24, 38] DDTs decreased most among the three types of pesticidal POPs with a up to 30-fold of reduction averagely from ~2000 pg/m^3 to ~70 pg/m^3. All DDT isomers were observed to decline with an order of magnitude, compared to the reported level in 2003-2004.[23] When comparing with other regions of China, the current DDT level in urban PRD region is at relatively low level, which is an order of magnitude lower than that in recent studies conducted in northern China[39] and other surrounding countries, including Nepal,[9] Pakistan[40] and Vietnam.[41]

Similar downtrend was observed for chlordane with an order of magnitude lower from 2000s[23] to now as indicated in Table S7. However, the declining trend appears to be slow down recently

with relatively stable level at ~200 pg/m^3 in the past decade.[38, 42] Chinese government banned chlordane production for all purposes in 2009. Its stable trend could possibly be caused by the gradually released from historical usage in building foundations and dams, which were extensively built during 1960s-1970s.[43] Furthermore, its present level in PRD is at an intermediate level, which is comparable to that in northern China[39] and other Asia countries.[41]

A stable trend was found for HCB, since HCB has never been used as a pesticide in China and is mainly from the unintentional production of combustion emissions, which is challenging for the effective control.[22] Our reported value is at medium level within China and across the world. It is much lower than that at the sites of northern and eastern China,[22, 39] but higher than that in Nam Co of Tibet (~20 pg/m^3). Internationally, the HCB in PRD region is much lower than that in Vietnam (~600 pg/m^3), but much higher than that in Pakistan (~30 pg/m^3) and Spain (~40 pg/m^3).

Source diagnostic ratios

DDT

Ratios of various DDT isomers offer useful source information. Firstly, ratios of DDT (sum of o,p'-DDT and p,p'-DDT)/ΣDDTs can be used to assess the long-term weathering and biotransformation of DDTs, since the p,p'-DDT principally degrades to p.p'- DDD and/or p.p'-DDE by microorganisms under anaerobic or aerobic conditions.[44] DDT/ΣDDTs ratios of >0.5 and <0.5 indicate the relatively "fresh" inputs and predominance of aged (microbially degraded) DDTs derived from the historical residues, respectively. But the boundary between "old" or "new" sources is not very clearly identified.[45] Our results suggested that the fresh DDT emission might still exist, given the observed high p,p'-DDT concertation and its percentage of 84±9% among DDTs, together with the high DDTs/DDEs ratio. Our study also observed much higher p,p'-DDT/p,p'-DDE ratios with an average value of 12±13, an order of magnitude higher than previous national study conducted in 2005.[37] o,p'-DDT metabolizes more readily than p,p'-DDT in the physical environment[46] and the degradation of technical DDT is unlikely to cause o,p'-DDT/p,p'-DDT higher than that in technical DDT.[17] In addition, high correlation among DDT isomers (R^2>0.90, p<0.01) possibly indicated that they were from similar sources.

The technical DDT was made up by p,p'-DDT (80-85%) and o,p'-DDT (15-20%), while the "dicofol-type DDT" was more dominated by o,p'-DDT.[17] The "dicofol-type DDT pollution" was defined as the DDT pollution caused by dicofol use and characterized with higher o,p'-DDT/p,p'-DDT concentration ratio (~7).[17] Therefore, the ratio of p,p'-DDT to ΣDDTs >0.8 could suggest the technical sources, whiles values <0.8 suggested the mixed sources of technical and dicofol-type DDT sources.[47] In our study, the ratios of p,p'-DDT/ΣDDTs were 0.63±0.09 and o,p-DDT/p,p'-DDT were 0.43±0.17, indicating technical and/or legacy technical DDT dominated with limited contribution from dicofol-type DDT.

Furthermore, we utilized the isomeric ratios of DDT to identify the possible source contribution, following the previous studies.[45, 48] This approach assumed the worst scenario as DDT in the environment only comes from dicofol formulation and technical DDT or antifouling painting and technical DDT. Because of the dominance of p,p'-DDT contributing>80% to the ΣDDTs, the fresh DDT should be the main source. Then it's reasonable to ignore the legacy DDTs. Due to very high correlation among isomers, DDTs should be probably from the same source.

Based on our rough estimation, if we assumed that only dicofol-type DDT and technical DDT exist, the dicofol-type DDT could contribute up to ~10% to the total sources, which is greatly lessened compared to previous study, as calculated from the reported value at ~50% in this region in 2003-2004.[48] It was reported that China has ceased to manufacture dicofol, to eliminate the DDT impurities in the dicofol in 2014 and later it was listed in the Stockholm Convention in 2019. This indicated the strong effectiveness with the implementation of Stockholm Convention. If we assumed that only antifouling painting produced DDT and technical DDT exist, around 30±50% DDT could be contributed by DDT-containing antifouling painting. The large standard deviation could possibly be caused by the random application of DDT-contained antifouling painting, indicating that it is not a fixed source. A seasonal pattern was also observed. Summer was contributed twice (~40%) by DDT from antifouling painting than that in winter (~20%).

Chlordane

TC/CC ratio is indicative of inputs from "weathered" (<1) or fresh (>1)chlordane sources.[37] The annual average TC/CC ratio in the air of the PRD region was 2.4±0.5 and presented very stable trend without seasonal difference (Kruskal-Wallis H Test, $p<0.001$). These ratios of TC/CC were observed to significantly increase, compared to previous studies with ratios of 0.3~1.4.[23] The ratios of TC/CC in technical chlordane are 1.3:1.1.[18] Elevated level indicated possibly continuous emission of chlordane in PRD. It is recorded that around 400-800 tons per year of chlordane were used in China.[2] Particularly in the PRD region, technical chlordane was extensively used against termites in buildings and dams.[23] Guangdong province is one of the major provincial-level administrative regions with ~8000 reservoir dams, mostly built during 1960s-1970s.[43] High ratio of TC/CC (>1) was also observed in the air of other Chinese regions, like the central China[49] and Tibet[50], and Vietnam.[41] CC was estimated to have shorter half-life than TC ($t_{1/2}$: 4.8 years versus 9.6 years),[51] which was unexpected, since TC was generally regarded as more susceptible to degradation by microorganism in soil.[52] A slightly increasing trend of TC/CC ratio was also revealed in the Arctic, which could possibly be caused by fresh usage of chlordane-based pesticides, like heptachlor.[51]

Seasonal coupling of sources and input pathways

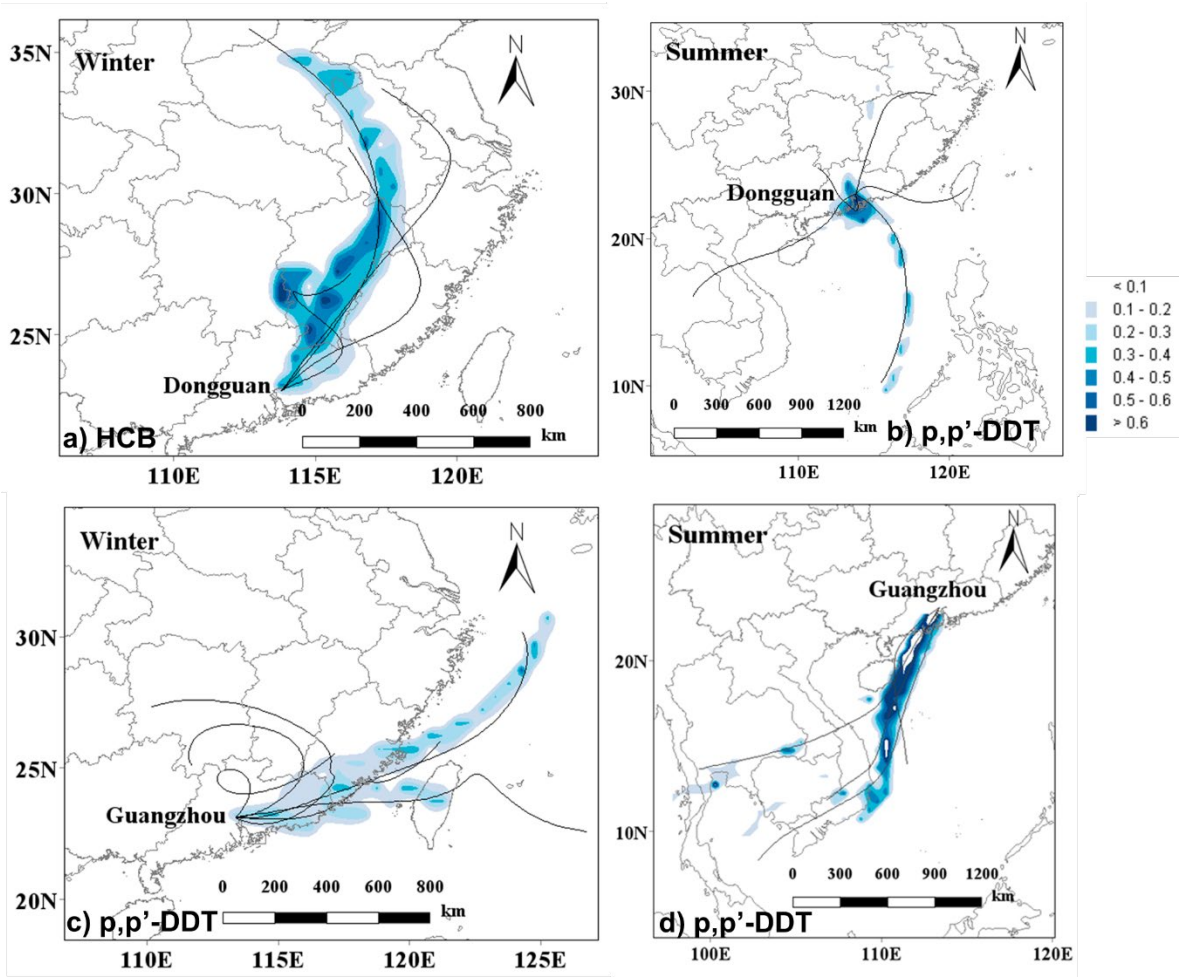
DDT

In order to understand the influence of monsoon and regional sources on the DDT, PSCF model results and distribution of air mass concentrations are presented in Figs. 2-3, based on 72 h backward trajectories from HYSPLIT model. During the sampling period, the Asian monsoon dominated in summer, while the winter monsoon was prevailing in winter as indicated in Fig. S2, which matches well with the DDT seasonality. Specifically, DDT concentration in summer was much higher than that in winter, which was possibly owing to primary and/or secondary emission from the coastal region. It was demonstrated that large parts of the tropical ocean and the southern mid-latitude ocean have turned net volatilization since the 1980s.[53, 54] As a result, DDT could continually re-enter the atmosphere from the ocean, before being dissolved again in a recurring cycle.[53] But this may be not the case here, since DDT was found to be highly

degraded (DDT/ΣDDTs<0.5) in the surface seawater of the South and East China Sea.[5, 54] On the contrary, detected DDT was much fresher in our air samples (DDT/ΣDDTs>0.7), which should be mainly from the primary sources instead of secondary sources from ocean.

The DDT-containing antifouling paint could be the potential ongoing primary emission. Our summer sampling time was within the period of annual fishing suspension (from May to August) in South China Sea region. During this period, many ships were moored at ports for maintenance (i.e. protective paint maintenance),[23] allowing a large amount of DDTs in the antifouling paint to enter the atmosphere.[55] Furthermore, those sampling sites closer to the ocean such as Zhuhai own higher DDT level and ratio of DDTs/HCB as shown in Fig. 1, , which indicated that DDT was likely sourced from the coastal region. Previous studies likewise demonstrated the ongoing usage of DDT-containing antifouling paints in the coastal region of China, with a decreased level of p,p'-DDT from the harbor to the inland.[5, 56]

Air masses of summer sampling periods mainly came from the South China Sea and then entered the PRD through the Pearl River estuary during Asian monsoon period (Fig. 3a-b). According to the PSCF results in Fig. 2, the source of DDT was mainly from the East China Sea, instead of the northern inland region. In winter, DDTs in Guangzhou was an order of magnitude higher than that in other sampling cities. When looking into the distribution of 24-h air mass concentrations in Guangzhou and Zhuhai in winter (Fig. 3c-d), it turned out that the air arrived in Guangzhou passed from East China Sea, while Zhuhai mainly received air masses from the northern inland. Also, mesoscale circulations, such as sea-land breezes (SLBs), play an important role in organic pollutants distribution and transport in the coastal cities.[57] Hence, we further confirmed that the monsoon transported from coast region greatly contributed DDT to the ambient air in PRD region. On the contrary, Wang *et al.* observed the opposite seasonality in Vietnam That is, the winter has higher DDT, mainly influenced by air mass from South China Sea in winter.[41] Therefore, Asian monsoon should be the main transport pathway for pesticidal POPs in PRD region.



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366 Figure 2. PSCF results of selected compounds in Dongguan and Zhuhai. Blacklines indicate
367 clustered 72 h backward trajectories from HYSPLIT model
368 (https://www.arl.noaa.gov/hysplit/hysplit/).

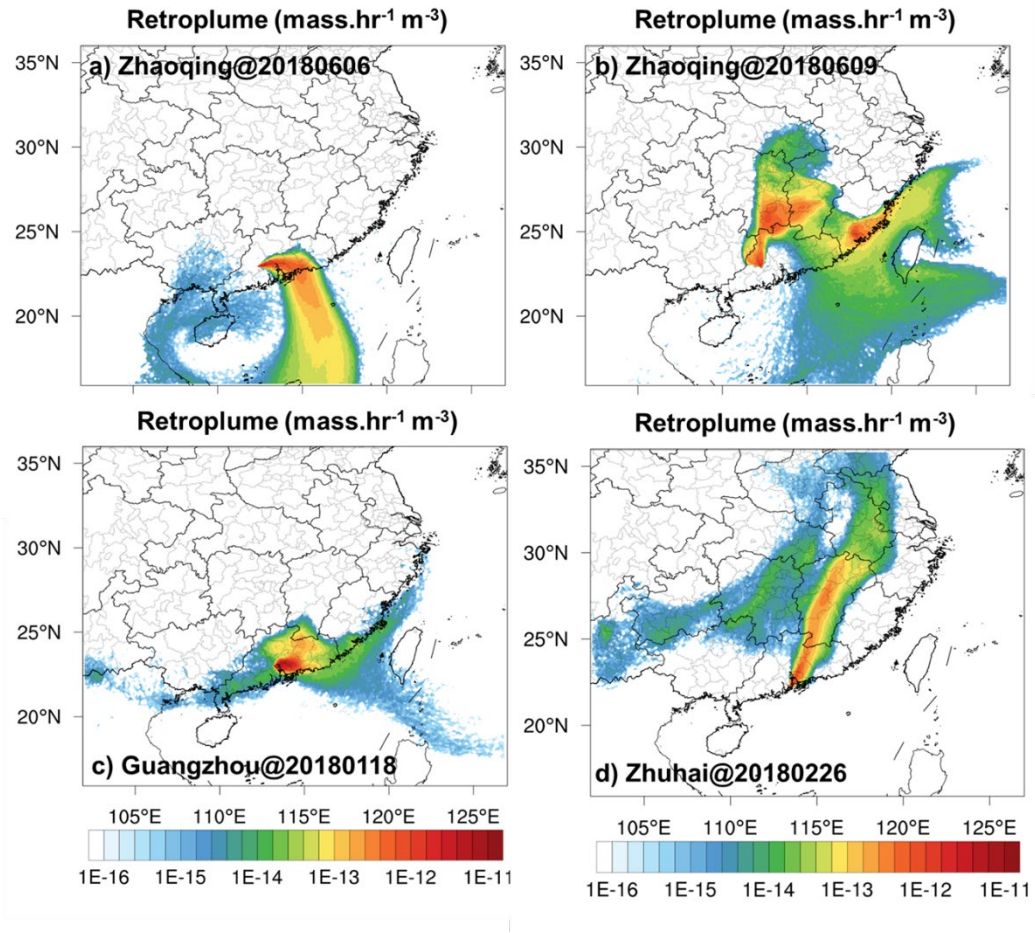

Figure 3. Model-simulated distribution of air mass concentration (mass h^{-1} m^{-3}) at the 500m height level simulated by HYSPLIT Lagrangian backward particle release model during 24h sampling period (https://www.arl.noaa.gov/hysplit/hysplit/).

Chlordane

Historically, technical chlordane was mixed with concrete and "locked" in foundations or dams to prevent termites during construction.[37] We observed more minor change of chlordane concentration between summer and winter than DDTs and HCB, much less influenced by temperature, implying slow kinetically controlled release of 'old' chlordane from the foundations/dams, rather than temperature-controlled evaporation from surface soil. Its widely varied concertation with two orders of magnitude difference, also indicated that it is mainly from scattered local point-source. An order of magnitude higher level of chlordane in PRD than that in northern China[39] and other Asian countries[40, 41] may suggest considerable amount of chlordane in the heavily termite-affected region of the PRD, which was regarded as one of the main regions extensively using chlordane in history. [19] Furthermore, PRD region was

used to largely build reservoir dams in 1960s-1970s, accounting for up to ~10% of the total documented dams built across China. Meantime, China started to produce chlordane in the 1950s on a pilot scale and reached an industrial scale in 1970s, the first peak production.[19] This would make large amount of chlordane locked inside the dams and/or buildings with a kinetically-controlled release since then.[43]

HCB

HCB in the PRD region is mainly received via winter monsoon with HCB combustion emission. Although HCB has never been used as a pesticide in China, it can be released as a trace contaminant from production and application of other pesticides and chemicals. Moreover, HCB can originate from incomplete combustion processes.[22] Its low summer/winter ratio of concentration (0.32±0.18) is the evidence of temperature-independence. This seasonal characteristic ruled out other sources except for thermal processes and combustion. Based on our PSCF results in Fig. 2a and Fig. S3, HCB in winter was mainly sourced from the northern China at all sampling sites, transported via the winter monsoon. In North China, a large amount of biofuels and fossil fuels are used for heating in winter, emitting high HCB.[39] This is most likely to explain the air-mass-led increase in HCB level during winter.[39] Also, lower mixing boundary layer height may increase pollutant concentration in winter.[58] In addition, HCB was less influenced by the winter monsoon compared to DDT, indicating that it is well-mixed in the ambient air. Its concentration was very stable without significant change, even when wind direction shifted from the north to the east (Fig. 3c).

Derived emission

Emission rates of selected OCPs in the PRD region derived from our model calculations for summer and winter are summarized in Table 2, in the units of per-capital and per-square emissions. Annual emissions in PRD were estimated based on two assumptions: 1) emissions remain constant for two half year in summer and winter; 2) emissions are directly proportional to the populations or land area in PRD. Combining the BETR-Global model with the measurements, the back-calculated total emissions of HCB, p,p'-DDT and chlordane in the region were 6.6 mg capital^{-1} year^{-1} and 71.8 μg m^{-2} year^{-1}, and the total emission rate was around ~4 t year^{-1} in the PRD region. For the seasonal emission pattern, HCB had two-fold emission in winter than that in summer, while p,p-DDT's emission in summer was an order of magnitude higher than that in winter. TC and CC had similar emission in winter and summer. All the emission seasonality of selected compounds was consistent with seasonal variation of measurements. The estimated emission rates made insignificant contribution to the nationally documented production (<1‰) summarized in Table 2, indicating the remarkable effectiveness under the adoption of Stockholm Convention. Larger contribution of chlordane to its historical production could be due to its later ban on all purpose usage in 2009.[19]

This study attempts to provide a snapshot on emission rates of selected OCPs in PRD under the worst-case scenario, combining atmospheric measurements and fugacity model. It is ideal to double-check and confirm our results with the "bottom-up" estimates or compare with other similar "top-down" modeling studies.[32] However, to our knowledge, relevant modelling work is very rare on pesticidal POPs and only limited study has been taken on their inventory development. *Wang et al.* established the inventory of technical chlordane productions between 1988 and 2008 across China, without congener-specific production estimates.[19] Historical inventory of DDT was also calculated, but its atmospheric concentration was not modelled[59]. Hence, comparison is impossible here. Challenge is severer for HCB, largely owing to its unintentional emissions, with limited knowledge on its sources and emission factors so far.

Table 2. Atmospheric emissions rates (median level) of selected OCP compounds in the PRD region.

Compound	Winter			Summer			Annual			
	kg d^{-1}	μg capital^{-1} d^{-1}[a]	ng m^{-2} d^{-1}[b]	kg d^{-1}	μg capital^{-1} d^{-1}	ng m^{-2} d^{-1}	kg $year^{-1}$	mg capital^{-1}$year^{-1}$	μg m^{-2} $year^{-1}$	%[c]
HCB	0.8	1.4	15.1	0.4	0.7	7.9	233	0.4	4.2	0.0003
p,p'-DDT	0.6	1.1	11.6	7.3	12.2	132.6	1457	2.4	26.3	0.0003
CC	2.3	3.9	42.4	1.6	2.6	28.3	715	1.2	12.9	0.05
TC	4.8	8.0	86.9	3.8	6.3	68.5	1571	2.6	28.4	
Sum	8.6	14.4	156.0	13.1	21.9	237.3	3975	6.6	71.8	0.006

[a]Based on a population of ca.6.0 x10^8 inhabitants in nine cities of the PRD region in 2018. [b]Based on the land area of 5.5 x10^{10} m^2 in the PRD region in 2018.[c] The percentage of annual emission to the total national documented production was calculated. The historical production was selected from literature for HCB[21], p,p'-DDT and chlordane.[60]

Limitations and implications

Although it has been proven to be useful previously,[32, 33] our back-calculation approach has several limitations. First of all, the estimated results highly relied on the quality and quantity of atmospheric measurements used to retrospectively model OCPs concentration in ambient air. Here, our observation sites are all located in urban area, which may lead to overestimated emissions. Secondly, as a worst-case scenario, the background concentration was only considered in the air, without inclusion in soil, water and sediment, while these compartments may also play a role of second source. Therefore, the actual emission is expected to be lower than our estimate. It is also noteworthy that our back-calculated emission was merely valid for the periods and locations of the field measurements and the spatial variability within the modelled region was not captured.

In terms of designed sampling campaign, it merely lasted two weeks respectively in winter and summer because of limited time and high labor cost. But this defect did not outweigh its merits. A snapshot of pesticidal POPs in the PRD region is integrated and presented under the view of geographic-anthropogenic scene. Our results clearly reflected the combined configuration of different sources, transport and fate of chemicals, leading to varied pollution characteristics, taking HCB, DDTs and chlordane as elegant examples. The unique coupling of summer monsoon with DDT-contained antifouling paint, winter monsoon with HCB combustion emission, as well as the historical 'sealed' chlordane, jointly presented the dynamic picture of these OCP compounds in the air of the PRD. Our study proposed a geographic-anthropogenic scenario, including source, history and air circulation patterns, which could be used exclusively to fully understand the fate of OCP compounds in a region.

Though effective reduction has been taken place, illegal technical DDT in antifouling paints for ships is still a problem. Dicofol-DDT is very likely to be diminished, particularly after the enlistment of dicofol by the Stockholm Convention in 2019. Release of chlordane in urban construction foundations and hydraulic dams is very slow due to kinetic control, which is a long-term challenge. HCB and other by-products as unintentionally-produced POPs from thermal processes will not fade out. These findings highlight the potentially ongoing sources of POPs, even after decades of regulations aimed at reducing or eliminating such sources.

Industries and communities should better manage thermal processes and combustion to gradually improve this situation. Long-term continuous sampling campaign will greatly help to assess the effectiveness of the implementation of the Stockholm Convention.

Supporting Information

Additional contents include the sampling information, instrumental method, detection limits, original concentration data and comparison with literature, backward trajectories and PSCF results.

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References

(1) UNEP *The Stockholm Convention on Persistent Organic Pollutants*; United Nations Environmental Programme: 2001.

(2) Wei, D.; Kameya, T.; Urano, K., Environmental management of pesticidal POPs in China: Past, present and future. *Environment International* **2007,** *33*, (7), 894-902.

(3) Zhang, G.; Parker, A.; House, A.; Mai, B. X.; Li, X. D.; Kang, Y. H.; Wang, Z. S., Sedimentary records of DDT and HCH in the Pearl River Delta, South China. *Environmental Science & Technology* **2002,** *36*, (17), 3671-3677.

(4) Wang, S.; Steiniche, T.; Romanak, K. A.; Johnson, E.; Quirós, R.; Mutegeki, R.; Wasserman, M. D.; Venier, M., Atmospheric Occurrence of Legacy Pesticides, Current Use Pesticides, and Flame Retardants in and around Protected Areas in Costa Rica and Uganda. *Environmental Science & Technology* **2019,** *53*, (11), 6171-6181.

(5) Ya, M.; Wu, Y.; Wu, S.; Li, Y.; Mu, J.; Fang, C.; Yan, J.; Zhao, Y.; Qian, R.; Lin, X.; Wang, X., Impacts of Seasonal Variation on Organochlorine Pesticides in the East China Sea and Northern South China Sea. *Environmental Science & Technology* **2019,** *53*, (22), 13088-13097.

(6) Zheng, Q.; Li, J.; Wang, Y.; Lin, T.; Xu, Y.; Zhong, G.; Bing, H.; Luo, C.; Zhang, G., Levels and

enantiomeric signatures of organochlorine pesticides in Chinese forest soils: Implications for sources and environmental behavior. *Environmental Pollution* **2020,** *262*, 114139.

(7) Taiwo, A. M., A review of environmental and health effects of organochlorine pesticide residues in Africa. *Chemosphere* **2019,** *220*, 1126-1140.

(8) Chen, W.; Jing, M.; Bu, J.; Ellis Burnet, J.; Qi, S.; Song, Q.; Ke, Y.; Miao, J.; Liu, M.; Yang, C., Organochlorine pesticides in the surface water and sediments from the Peacock River Drainage Basin in Xinjiang, China: a study of an arid zone in Central Asia. *Environmental Monitoring and Assessment* **2011,** *177*, (1), 1-21.

(9) Gong, P.; Wang, X.; Pokhrel, B.; Wang, H.; Liu, X.; Liu, X.; Wania, F., Trans-Himalayan Transport of Organochlorine Compounds: Three-Year Observations and Model-Based Flux Estimation. *Environmental Science & Technology* **2019,** *53*, (12), 6773-6783.

(10) Ren, J.; Wang, X.; Gong, P.; Wang, C., Characterization of Tibetan Soil As a Source or Sink of Atmospheric Persistent Organic Pollutants: Seasonal Shift and Impact of Global Warming. *Environmental Science & Technology* **2019,** *53*, (7), 3589-3598.

(11) Carrizo, D.; Sobek, A.; Salvadó, J. A.; Gustafsson, Ö., Spatial Distributions of DDTs in the Water Masses of the Arctic Ocean. *Environmental Science & Technology* **2017,** *51*, (14), 7913-7919.

(12) Bravo, N.; Grimalt, J. O.; Chashchin, M.; Chashchin, V. P.; Odland, J.-O., Drivers of maternal accumulation of organohalogen pollutants in Arctic areas (Chukotka, Russia) and 4,4 '-DDT effects on the newborns. *Environment International* **2019,** *124*, 541-552.

(13) Lin, T.; Hu, Z.; Zhang, G.; Li, X.; Xu, W.; Tang, J.; Li, J., Levels and Mass Burden of DDTs in Sediments from Fishing Harbors: The Importance of DDT-Containing Antifouling Paint to the Coastal Environment of China. *Environmental Science & Technology* **2009,** *43*, (21), 8033-8038.

(14) Schenker, U.; Scheringer, M.; Hungerbühler, K., Investigating the Global Fate of DDT: Model Evaluation and Estimation of Future Trends. *Environmental Science & Technology* **2008,** *42*, (4), 1178-1184.

(15) Manaca, M. N.; Grimalt, J. O.; Gari, M.; Sacarlal, J.; Sunyer, J.; Gonzalez, R.; Dobano, C.; Menendez, C.; Alonso, P. L., Assessment of exposure to DDT and metabolites after indoor residual spraying through the analysis of thatch material from rural African dwellings. *Environmental Science and Pollution Research* **2012,** *19*, (3), 756-762.

(16) Manaca, M. N.; Grimalt, J. O.; Sunyer, J.; Mandomando, I.; Gonzalez, R.; Sacarlal, J.; Dobano, C.; Alonso, P. L.; Menendez, C., Concentration of DDT compounds in breast milk from African women (Manhica, Mozambique) at the early stages of domestic indoor spraying with this insecticide. *Chemosphere* **2011,** *85*, (3), 307-314.

(17) Qiu, X. H.; Zhu, T.; Yao, B.; Hu, J. X.; Hu, S. W., Contribution of dicofol to the current DDT pollution in China. *Environmental Science & Technology* **2005,** *39*, (12), 4385-4390.

(18) Bidleman, T. F.; Jantunen, L. M. M.; Helm, P. A.; Brorström-Lundén, E.; Juntto, S., Chlordane Enantiomers and Temporal Trends of Chlordane Isomers in Arctic Air. *Environmental Science & Technology* **2002,** *36*, (4), 539-544.

(19) Wang, Q.; Zhao, L.; Fang, X.; Xu, J.; Li, Y.; Shi, Y.; Hu, J., Gridded usage inventories of chlordane in China. *Frontiers of Environmental Science & Engineering* **2013,** *7*, (1), 10-18.

(20) Bailey, R. E., Global hexachlorobenzene emissions. *Chemosphere* **2001,** *43*, (2), 167-182.

(21) Wang, G.; Lu, Y.; Han, J.; Luo, W.; Shi, Y.; Wang, T.; Sun, Y., Hexachlorobenzene sources, levels and human exposure in the environment of China. *Environ Int* **2010,** *36*, (1), 122-130.

(22) Mao, S.; Zhang, G.; Li, J.; Geng, X.; Wang, J.; Zhao, S.; Cheng, Z.; Xu, Y.; Li, Q.; Wang, Y., Occurrence and sources of PCBs, PCNs, and HCB in the atmosphere at a regional background site in east China: Implications for combustion sources. *Environmental Pollution* **2020,** *262*, 114267.

(23) Li, J.; Zhang, G.; Guo, L.; Xu, W.; Li, X.; Lee, C. S. L.; Ding, A.; Wang, T., Organochlorine pesticides in the atmosphere of Guangzhou and Hong Kong: Regional sources and long-range atmospheric transport. *Atmospheric Environment* **2007,** *41*, (18), 3889-3903.

(24) Wang, J.; Guo, L.; Li, J.; Zhang, G.; Lee, C. S. L.; Li, X.; Jones, K. C.; Xiang, Y.; Zhong, L., Passive air sampling of DDT, chlordane and HCB in the Pearl River Delta, South China: Implications to regional sources. *Journal of Environmental Monitoring* **2007,** *9*, (6), 582-588.

(25) Liu, L., The Water-Economy Nexus and Sustainable Transition of the Pearl River Delta, China (1999–2015). *Sustainability* **2018,** *v. 10*, (no. 8), 2018 v.10 no.8.

(26) Statistics Bureau of Guangdong Province *Analysis of population development in guangdong of 2019 (in Chinese)*; 2019.

(27) Zeren, Y.; Guo, H.; Lyu, X.; Jiang, F.; Wang, Y.; Liu, X.; Zeng, L.; Li, M.; Li, L., An Ozone "Pool" in South China: Investigations on Atmospheric Dynamics and Photochemical Processes Over the Pearl River Estuary. *Journal of Geophysical Research: Atmospheres* **2019,** *124*, (22), 12340-12355.

(28) Ding, A.; Wang, T.; Fu, C., Transport characteristics and origins of carbon monoxide and ozone in Hong Kong, South China. *Journal of Geophysical Research: Atmospheres* **2013,** *118*, (16), 9475-9488.

(29) Wang, H.; Lyu, X.; Guo, H.; Wang, Y.; Zou, S.; Ling, Z.; Wang, X.; Jiang, F.; Zeren, Y.; Pan, W.; Huang, X.; Shen, J., Ozone pollution around a coastal region of South China Sea: interaction between marine and continental air. *Atmospheric Chemistry and Physics* **2018,** *18*, (6), 4277-4295.

(30) Wang, X.; Zong, Z.; Tian, C.; Chen, Y.; Luo, C.; Tang, J.; Li, J.; Zhang, G., Assessing on toxic potency of PM2.5-bound polycyclic aromatic hydrocarbons at a national atmospheric

566 background site in North China. *Science of The Total Environment* **2018,** *612*, 330-338.

567 (31) Geng, X.; Mo, Y.; Li, J.; Zhong, G.; Tang, J.; Jiang, H.; Ding, X.; Malik, R. N.; Zhang, G., Source
568 apportionment of water-soluble brown carbon in aerosols over the northern South China Sea:
569 Influence from land outflow, SOA formation and marine emission. *Atmospheric Environment*
570 **2020,** *229*, 117484.

571 (32) Bogdal, C.; Muller, C. E.; Buser, A. M.; Wang, Z. Y.; Scheringer, M.; Gerecke, A. C.; Schmid,
572 P.; Zennegg, M.; MacLeod, M.; Hungerbuhler, K., Emissions of Polychlorinated Biphenyls,
573 Polychlorinated Dibenzo-p-dioxins, and Polychlorinated Dibenzofurans during 2010 and 2011
574 in Zurich, Switzerland. *Environmental Science & Technology* **2014,** *48*, (1), 482-490.

575 (33) Rodgers, T. F. M.; Truong, J. W.; Jantunen, L. M.; Helm, P. A.; Diamond, M. L.,
576 Organophosphate Ester Transport, Fate, and Emissions in Toronto, Canada, Estimated Using an
577 Updated Multimedia Urban Model. *Environmental Science & Technology* **2018,** *52*, (21),
578 12465-12474.

579 (34) Zhao, S.; Breivik, K.; Liu, G.; Zheng, M.; Jones, K. C.; Sweetman, A. J., Long-Term Temporal
580 Trends of Polychlorinated Biphenyls and Their Controlling Sources in China. *Environmental*
581 *Science & Technology* **2017,** *51*, (5), 2838-2845.

582 (35) MacLeod, M.; Riley, W. J.; McKone, T. E., Assessing the Influence of Climate Variability on
583 Atmospheric Concentrations of Polychlorinated Biphenyls Using a Global-Scale Mass Balance
584 Model (BETR-Global). *Environmental Science & Technology* **2005,** *39*, (17), 6749-6756.

585 (36) Wöhrnschimmel, H.; MacLeod, M.; Hungerbuhler, K., Emissions, Fate and Transport of
586 Persistent Organic Pollutants to the Arctic in a Changing Global Climate. *Environmental Science*
587 *& Technology* **2013,** *47*, (5), 2323-2330.

588 (37) Liu, X.; Zhang, G.; Li, J.; Yu, L. L.; Xu, Y.; Li, X. D.; Kobara, Y.; Jones, K. C., Seasonal Patterns
589 and Current Sources of DDTs, Chlordanes, Hexachlorobenzene, and Endosulfan in the
590 Atmosphere of 37 Chinese Cities. *Environmental Science & Technology* **2009,** *43*, (5), 1316-
591 1321.

592 (38) Yang, Y.; Li, D.; Mu, D., Levels, seasonal variations and sources of organochlorine pesticides
593 in ambient air of Guangzhou, China. *Atmospheric Environment* **2008,** *42*, (4), 677-687.

594 (39) Yu, S. Y.; Liu, W. J.; Xu, Y. S.; Zhao, Y. Z.; Cai, C. Y.; Liu, Y.; Wang, X.; Xiong, G. N.; Tao, S.; Liu,
595 W. X., Organochlorine pesticides in ambient air from the littoral cities of northern China:
596 Spatial distribution, seasonal variation, source apportionment and cancer risk assessment. *Sci*
597 *Total Environ* **2019,** *652*, 163-176.

598 (40) Syed, J. H.; Malik, R. N.; Liu, D.; Xu, Y.; Wang, Y.; Li, J.; Zhang, G.; Jones, K. C., Organochlorine
599 pesticides in air and soil and estimated air–soil exchange in Punjab, Pakistan. *Science of The*
600 *Total Environment* **2013,** *444*, 491-497.

601 (41) Wang, W. T.; Wang, Y. H.; Zhang, R. J.; Wang, S. P.; Wei, C. S.; Chaemfa, C.; Li, J.; Zhang, G.;

Yu, K. F., Seasonal characteristics and current sources of OCPs and PCBs and enantiomeric signatures of chiral OCPs in the atmosphere of Vietnam. *Science of The Total Environment* **2016,** *542*, 777-786.

(42) Li, Z.; Zhou, Z.; Gu, T.; Li, S.; Zhang, S.; Liu, D., Organochloride pesticides in the atmosphere of Shenzhen in winter and summer. *China Environmental Science* **2011,** *31*, (05), 724-728.

(43) Yuan, M.; Xu, Y.; Li, S.; Zhang, X.; Pan, Z., Safety evaluation and analysis of small-scale reservoir in Guangdong. *Dam and Safety* **2019,** *4*, 20-23.

(44) Yu, H.-Y.; Bao, L.-J.; Liang, Y.; Zeng, E. Y., Field Validation of Anaerobic Degradation Pathways for Dichlorodiphenyltrichloroethane (DDT) and 13 Metabolites in Marine Sediment Cores from China. *Environmental Science & Technology* **2011,** *45*, (12), 5245-5252.

(45) Zhang, C.; Liu, L.; Ma, Y.; Li, F., Using Isomeric and Metabolic Ratios of DDT To Identify the Sources and Fate of DDT in Chinese Agricultural Topsoil. *Environmental Science & Technology* **2018,** *52*, (4), 1990-1996.

(46) Martijn, A.; Bakker, H.; Schreuder, R. H., SOIL PERSISTENCE OF DDT, DIELDRIN, AND LINDANE OVER A LONG-PERIOD. *Bulletin of Environmental Contamination and Toxicology* **1993,** *51*, (2), 178-184.

(47) Wu, Y.; Wang, X.; Ya, M.; Li, Y.; Hong, H., Distributions of organochlorine compounds in sediments from Jiulong River Estuary and adjacent Western Taiwan Strait: Implications of transport, sources and inventories. *Environmental Pollution* **2016,** *219*, 519-527.

(48) Qiu, X.; Zhu, T., Using the o,p′-DDT/p,p′-DDT ratio to identify DDT sources in China. *Chemosphere* **2010,** *81*, (8), 1033-1038.

(49) Zhan, L.; Lin, T.; Wang, Z.; Cheng, Z.; Zhang, G.; Lyu, X.; Cheng, H., Occurrence and air-soil exchange of organochlorine pesticides and polychlorinated biphenyls at a CAWNET background site in central China: Implications for influencing factors and fate. *Chemosphere* **2017,** *186*, 475-487.

(50) Li, J.; Lin, T.; Qi, S.; Zhang, G.; Liu, X.; Li, K., Evidence of local emission of organochlorine pesticides in the Tibetan plateau. *Atmospheric Environment* **2008,** *42*, (32), 7397-7404.

(51) Hung, H.; Halsall, C. J.; Blanchard, P.; Li, H. H.; Fellin, P.; Stern, G.; Rosenberg, B., Temporal Trends of Organochlorine Pesticides in the Canadian Arctic Atmosphere. *Environmental Science & Technology* **2002,** *36*, (5), 862-868.

(52) Beeman, R. W.; Matsumura, F., Metabolism of cis- and trans-chlordane by a soil microorganism. *Journal of Agricultural and Food Chemistry* **1981,** *29*, (1), 84-89.

(53) Stemmler, I.; Lammel, G., Cycling of DDT in the global environment 1950–2002: World ocean returns the pollutant. *Geophysical Research Letters* **2009,** *36*, (24).

(54) Wu, Z.; Lin, T.; Hu, L.; Guo, T.; Guo, Z., Atmospheric legacy organochlorine pesticides and their recent exchange dynamics in the Northwest Pacific Ocean. *Science of The Total Environment* **2020**, 138408.

(55) Tian Lin, Z. H., Gan Zhang, XiangDong Li, Weihai Xu, Jianhui Tang,Jun Li <Levels and Mass Burden of DDTs in Sediments from Fishing Harbors-The Importance of DDT-Containing Antifouling Paint to the Coastal Environment of China.pdf>. **2009**.

(56) Yu, H.-Y.; Shen, R.-L.; Liang, Y.; Cheng, H.; Zeng, E. Y., Inputs of antifouling paint-derived dichlorodiphenyltrichloroethanes (DDTs) to a typical mariculture zone (South China): Potential impact on aquafarming environment. *Environmental Pollution* **2011,** *159*, (12), 3700-3705.

(57) Lo, J. C. F.; Lau, A. K. H.; Fung, J. C. H.; Chen, F., Investigation of enhanced cross-city transport and trapping of air pollutants by coastal and urban land-sea breeze circulations. *Journal of Geophysical Research: Atmospheres* **2006,** *111*, (D14).

(58) Dumanoglu, Y.; Gaga, E. O.; Gungormus, E.; Sofuoglu, S. C.; Odabasi, M., Spatial and seasonal variations, sources, air-soil exchange, and carcinogenic risk assessment for PAHs and PCBs in air and soil of Kutahya, Turkey, the province of thermal power plants. *Science of The Total Environment* **2017,** *580*, 920-935.

(59) Li, Y.-F.; Cai, D. J.; Singh, A., Historical DDT use trend in China and usage data gridding with 1/4° by 1/6° longitude/latitude resolution. *Adv. Environ. Res.* **1999,** *2*, 497-506.

(60) Zhao, L. Usage Inventories for Selected Persistent Organic Pollutants in China. Peking University, Beijing, 2005.